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Externally Driven Molecular Ratchets on a Periodic Potential Surface: a Rate Equations Approach

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Abstract

A long time dynamics of molecular ratchets on a 1D periodic potential energy surface (PES) subjected to an external stimulus is studied using the rate equations method. The PES consisting of repeated waveforms made of two peaks is considered as an example of a spatially symmetric or asymmetric PES. That PES may, e.g., correspond to a diffusion of a bipedal molecule that moves along an atomic track via an inchworm walk mechanism [Angewandte Chemie Int. Ed. **54**, 7101 (2015)]. A generalisation to a PES consisting of an arbitrary number of peaks of various heights is straightforward. Assuming the validity of the transition state theory (TST) for the calculation of the transition rates between neighbouring potential wells, probabilities of occupying each type of the potential well on the PES is obtained analytically, and then the net current for the molecules to move preferentially in a particular direction under a selection of external fields at long time is derived. Note that at variance with methods based on solving numerically the corresponding Fokker-Plank equation, our method is entirely analytical in the limit of weak external fields. Results of the analytical calculations are compared with the exact numerical solution of the derived rate equations. The following external stimuli are considered: a constant, sinusoidal and shifted sinusoidal fields due to either a spatially uniform thermal gradient or electrostatic field. Possible applications of the method for extracting energy from Brownian motion under load and separating molecules of different chirality on the surface are also discussed.

Introduction

Various applications such as purification of mixtures, separation of molecules, sensors, etc. require development of new methods for controlling molecular diffusion on surfaces. This direction of research is attributed to an exciting field of molecular motors or ratchets[1–5], which has become a topic of significant interest in chemistry and physics. Notable examples of such ratchets are molecular motors such as kinesin[6], myosin[7] or dynein[8] that, driven by a chemical reaction, can walk along one-dimensional tracks in the cells performing specific tasks[4,5]. Many more examples of such ratchets are known (see the reviews cited above) in both organic and inorganic sciences where unidirectional motion of the ratchets is stimulated by external fields, temperature gradient,

light, chemical reactions or a combination of these.

Fundamental principles governing diffusion of molecules under different external stimuli (or the absence of those) are well understood[3–5,9–11]. In thermal equilibrium a Brownian particle placed in a 1D periodic potential of a lattice would diffuse in both directions (to the 'right' and 'left') with the same probability. This statement is valid no matter whether the waveform, the repetition of which comprises the corresponding potential energy surface (PES), is spatially symmetric or asymmetric. This is due to the principle of detailed balance, as otherwise the second law of thermodynamics would be violated. To enforce diffusion in a particular direction and therefore create a unidirectional net transport, one has to break thermal equilibrium, e.g., by applying an external stimulus such as external fields[12,13] or temperature fluctuations[14,15]. If the external stimulus is time-dependent and of zero mean, however, unidirectional movement requires a broken spatial symmetry, e.g. manifested by an asymmetric periodic waveforms in the PES.

To the best of our knowledge, mainly the Fokker-Plank equation method[3–5,10] has been widely used in theoretical studies on Brownian ratchets. Apart from some simple examples, investigations of specific external fields require numerical solutions of this partial differential equation. Recently we proposed a kinetic Monte Carlo approach to study Brownian molecular ratchets on surfaces[16] which has an advantage of considering realistic molecules and surfaces at reasonable computational time. In this paper we propose an alternative approach, a simple method based on rate equations, which numerically is even more advantageous. Moreover, for an external field of an oscillatory time dependence this new method provides an *analytical* expression for the net current assuming that the perturbation due to the field can be considered perturbatively, i.e. the field is 'weak' as compared to the characteristic energy barriers in the system and the thermal energy k_BT. In this way more complex time dependencies may also be at reach. Having an analytical solution enables one to analyse the behaviour of molecules on surfaces directly, without performing numerical calculations, based entirely on the shape of their PES. The analytical solutions are compared with the (exact) numerical solutions which can be used for any strength of the field.

In the next section we shall present our general theory, while in the following section various examples of the external field will be considered, expressions for the net current derived and the

appropriate numerical simulations presented. Then a discussion will be given, and we finish with conclusions.

Theory

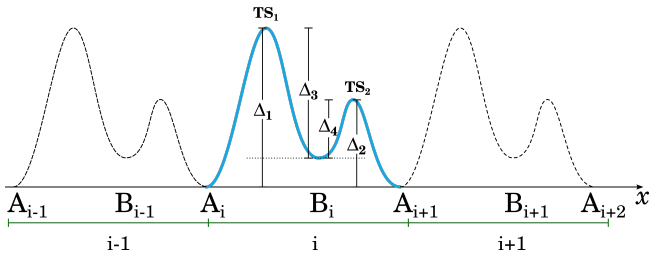

Figure 1: The 1D PES considered here consists of a periodically repeated waveforms (blue). Each waveform is composed of two peaks of (generally) different heights with the energy barriers from Δ_1 to Δ_4. Each waveform is numbered by the index i and has two distinct energy minima designated A and B.

Consider a 1D potential energy surface (PES) composed by an infinite repetition of identical waveforms each consisting of two peaks, Fig. 1. This PES can be viewed as an infinite repetition of two potential energy minima, A (the ground state) and B (the metastable state). A consideration of more complicated waveforms containing more than two peaks is straightforward and won't be disscussed here. Within the Harmonic Transition State Theory (HTST)[17,18], the transition rate for jumping from A to B in the direction to the right is $k_{A\rightarrow} = \nu_A \exp(-\beta\Delta_1)$, while in the direction to the left it is $k_{A\leftarrow} = \nu_A \exp(-\beta\Delta_2)$. Similarly, the rate for jumping to either of the two A states to the right and to the left from the state B are $k_{B\rightarrow} = \nu_B \exp(-\beta\Delta_4)$ and $k_{B\leftarrow} = \nu_B \exp(-\beta\Delta_3)$, respectively. Here ν_A and ν_B are the prefactors (attempt frequencies), $\beta = 1/k_B T$ the inverse temperature, and Δ_i $(i = 1, \ldots, 4)$ the energy barriers that are shown in the Figure. Note that a spatially asymmetric waveform requires, within the HTST, at least two peaks to be present. Such a PES corresponds, e.g., to a bipedal molecule diffusing along a single direction by means of the inchworm mechanism[16,19], so that the first peak (to the right from A to B) corresponds to the molecule stepping with its back 'foot' to the right, while the second peak corresponds to the front 'foot' stepping in the same direction, thereby displacing the molecule by one lattice constant.

We are interested here in studying the time evolution of molecules initially distributed some-

where on the 1D lattice of these periodic potential wells. Let $p_{A,i}(t)$ and $p_{B,i}(t)$ be the probabilities to find the molecule in the wells A and B of the waveform i, respectively. Then, the rate equations for the dynamics of the molecule read:

$$\dot{p}_{A,i} = k_{B\rightarrow} p_{B,i-1} + k_{B\leftarrow} p_{B,i} - \left(k_{A\rightarrow} + k_{A\leftarrow}\right) p_{A,i} \tag{1}$$

$$\dot{p}_{B,i} = -\left(k_{B\rightarrow} + k_{B\leftarrow}\right) p_{B,i} + k_{A\rightarrow} p_{A,i} + k_{A\leftarrow} p_{A,i+1} \tag{2}$$

where the dot above a letter corresponds to the time derivative. This set of equations is infinite as it is to be written for each waveform i. Overall probabilities of the sites A and B are given by the sums $p_A(t) = \sum_i p_{A,i}(t)$ and $p_B(t) = \sum_i p_{B,i}(t)$. Their equations of motion are obtained by summing up the equations above for each value of i:

$$\dot{p}_A = k_B p_B - k_A p_A \quad \text{and} \quad \dot{p}_B = -k_B p_B + k_A p_A \tag{3}$$

where $k_B = k_{B\rightarrow} + k_{B\leftarrow}$ and $k_A = k_{A\rightarrow} + k_{A\leftarrow}$ are the corresponding escape rates from the states B and A, respectively. As expected, $p_A + p_B$ does not depend on time and is equal to one. Correspondingly, the above equations can be written as a single equation

$$\dot{p}_A + \kappa(t) p_A = k_B \tag{4}$$

whose solution, satisfying the initial condition $p_A(0) = 1$, corresponding to the molecules being initially on sites A (at long times the choice of the initial condition is not important), is:

$$p_A(t) = \exp\left(-\int_0^t \kappa(\tau)\, d\tau\right) + \int_0^t k_B(\tau') \exp\left(-\int_{\tau'}^t \kappa(\tau)\, d\tau\right) d\tau' \tag{5}$$

where

$$\kappa(t) = k_A + k_B = k_{A\rightarrow} + k_{A\leftarrow} + k_{B\rightarrow} + k_{B\leftarrow} \tag{6}$$

Note that a different initial condition would correspond to a non-unit prefactor to the first (ex-

ponential) term in the right hand side of the solution for $p_A(t)$, which at long times disappears anyway.

The net flux (current) of molecules to the right can be calculated as a difference of the fluxes to the right and to the left,

$$j_{\rightarrow} = p_A k_{A\rightarrow} + p_B k_{B\rightarrow} \quad \text{and} \quad j_{\leftarrow} = p_A k_{A\leftarrow} + p_B k_{B\leftarrow} \,, \tag{7}$$

and is given by:

$$j(t) = j_{\rightarrow}(t) - j_{\leftarrow}(t) = (k_{B\rightarrow} - k_{B\leftarrow}) + (k_{A\rightarrow} - k_{A\leftarrow} - k_{B\rightarrow} + k_{B\leftarrow})\, p_A \tag{8}$$

where the identity $p_A + p_B = 1$ has been used. If the net flux is positive, the molecules on average move preferentially to the right, if negative, to the left.

Note that energy barriers Δ_i depend on the external stimulus applied to the system and, in particular, will depend on time if the external stimulus is time dependent. Two types of such stimuli can be easily simulated: (i) an electrostatic field and (ii) a temperature gradient [16].

In the first case the molecule is to be charged and then a spatially uniform electric field $E(t)$ (in units of energy over distance) would create an additional electrostatic potential, $\Delta U(x,t) = -E(t)x$, changing linearly with the coordinate x along our 1D system. This extra potential will affect the energy barriers in a certain way, as it would tilt the PES one way or another, depending on the field direction. Indeed, the energies of the minima A and B and of the saddle points TS_1 and TS_2 will be modified. This in turn will affect the values of the energy barriers as clearly the energies at the minima and the saddle points will be shifted by different amounts. To be more specific, we choose one waveform in which positions of the state A, saddle point between A and B, state B, as well as the saddle point between B and the next A (in the direction to the right in Fig. 1) be $x = 0$, $a/4$, $a/2$, $3a/4$ and a, respectively, where a is the distance between two nearest minima A (the lattice constant). Then the relative shift of the first saddle point to the right of A at $x = 0$ is $-aE/4$, the minimum B is shifted by $-aE/2$, and so on. It is easy to see then that the following expressions for the energy barriers in the presence of the field are obtained:

$\Delta_1 = \Delta_1^0 - aE/4$, $\Delta_2 = \Delta_2^0 + aE/4$, $\Delta_3 = \Delta_3^0 + aE/4$ and $\Delta_4 = \Delta_4^0 - aE/4$, where Δ_i^0 are the barriers without the field. We observe that the effect of the field is such that the barriers in the direction of the field are reduced, while in the opposite direction increased. For simplicity, we shall consider the prefactors to the four rates identical and equal to ν, we shall also assume that they are not affected by the field as the effect of the energy barriers on the rates is much more important than of the prefactors. In realistic calculations these simplifications can be easily lifted.

In the second case (the temperature gradient) the energy barriers effectively change in the same way if the temperature gradient, $g_T = \nabla_x T(x)$, is spatially uniform (does not depend on x) and small. Indeed, in this case the temperature $T(x) = T_0 + g_T x$ depends linearly on x, and hence each rate, for small gradients, can be approximately written as

$$k_i = \nu \exp\left(-\frac{\Delta_i}{k_B\left(T_0 + g_T x\right)}\right) \simeq \nu \exp\left(-\beta_0 \Delta_i(x)\right) \tag{9}$$

where $\beta_0 = 1/k_B T_0$ and $\Delta_i(x) = \Delta_i\left(1 - g_T x/T_0\right)$ is an effective barrier that linearly depends on x. Hence, in this case the barriers Δ_i will change in a similar way as in the first case: the effect of this stimulus is that the effective energy barriers in the direction of the temperature gradient (assuming $g_T > 0$, i.e. in the direction of the increase of the temperature) are increased, while those in the opposite direction reduced. Note that we assume here that $g_T \ll T_0/\xi$, where ξ is a characteristic distance over which a molecule may diffuse on the surface (the length of the molecule's track) and T_0 is the temperature in the middle of the track.

Even though in the case of the temperature gradient an effective field $E = g_T\overline{\Delta}/T_0$ can only be defined approximately via an average barrier $\overline{\Delta}$, to simplify the consideration we shall treat both cases on the same footing by assuming that an external effective field E acts causing the following changes to the barriers: $\Delta_{1,4} = \Delta_{1,4}^0 - aE/4$ and $\Delta_{2,3} = \Delta_{2,3}^0 + aE/4$. Correspondingly, the individual rates depend on the field via $k_{A\rightarrow} = k_{A\rightarrow}^0 e^{\lambda_1}$, $k_{B\rightarrow} = k_{B\rightarrow}^0 e^{\lambda_1}$, $k_{A\leftarrow} = k_{A\leftarrow}^0 e^{-\lambda_1}$ and $k_{B\leftarrow} = k_{B\leftarrow}^0 e^{-\lambda_1}$, where $\lambda_1 = E\beta a/4$ directly depends on the field and temperature. Clearly, as the field depends on time, so are the barriers and hence the rates. Here and in the following the zero subscript or superscript indicates the values of the quantities (e.g. barriers and rates) without the field.

In what follows, we shall consider the fields changing in time, and hence the net flux (or current) of Eq. (8) becomes time dependent. To simplify our treatment, we shall be considering in this work only either constant or time periodic external fields with the characteristic time $\mathcal{T}$ (a period in the latter case), and hence will be interested in the values of the current averaged over that time, calculated at long observation times:

$$j_{av} = \lim_{t\to\infty} \frac{1}{\mathcal{T}} \int_t^{t+\mathcal{T}} j(t)dt \tag{10}$$

Equations (5)-(10) written above enable one to calculate the average net flux exactly provided that we know how the transition rates depend on the applied field. We shall apply these equations to several types of the external field of practical interest: (i) constant, (ii) sinusoidal and (iii) shifted sinusoidal fields. Only in the first case the net current can be analytically worked out exactly, in the latter two cases an analytical calculation can only be performed approximately in the limit of weak external fields. Still, in those two cases the results can be compared with a numerical method, based on the numerical solution of the rate equation (4). This has been done simply by choosing a small time step τ and iterating the equation via

$$p_A(t+\tau) = p_A(t) + [k_B(t) - \kappa(t)p_A(t)]\,\tau \tag{11}$$

where $p_A(0) = 1$, and then taking the results at long times (the stationary limit).

Even though our treatment is general, in order to be specific, results of analytical and numerical calculations described below are given having a realistic molecule in mind, 1,3-bis(imidazol-1-ylmethyl)-5(1-phenylethyl)benzene (or BIPEB for short)[16], see the inset to Fig. 2, where its R enantiomer is shown. The molecule is adsorbed on the Cu(110) surface. The surface consists of parallel rows of protruding Cu atoms, and the molecule adsorbs on this surface by attaching to two Cu atoms of the same Cu row with its imidazol groups serving as its feet. The diffusion of the BIPEB molecule on the surface happens preferentially along (rather than across) the rows via the inchworm mechanism[19] whereby the molecule first steps with its rear and then with the front foot. Correspondingly, the PES of the molecule on the Cu(110) surface along a Cu row consists of

a periodic repetition of a waveform comprised of two peaks as in Fig. 1 with the calculated energy barriers Δ_1^0 =0.339 eV, Δ_2^0 =0.316 eV, Δ_3^0 =0.170 eV and Δ_4^0 =0.147 eV[16]. Numerical results below are presented in units in which the lattice constant of the Cu row is chosen to be $a = 1$ Å.

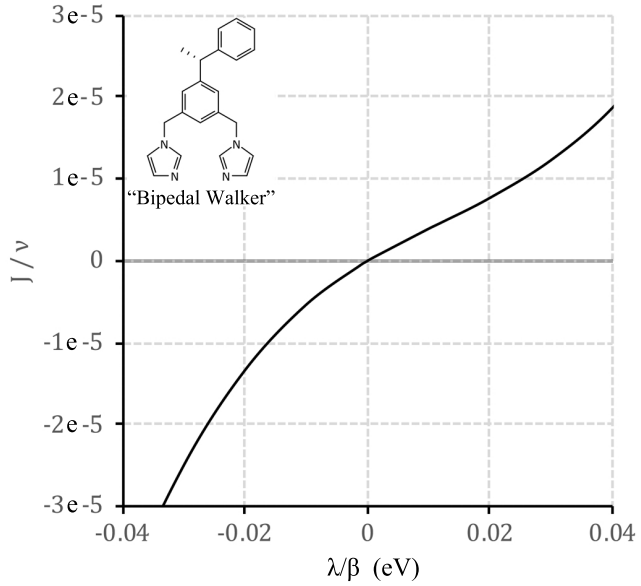

Figure 2: The net current (in units of the rate prefactor ν) for the BIPEB molecule (inset) as a function of the constant field, λ/β, at the temperature T =300 K.

Results and Discussion

Zero and constant field

Let us first consider our system with a constant external field being applied. In this case the rates do not depend on time, and the whole calculation can be performed exactly. We obtain:

$$j_{av} = \frac{2}{\kappa}\left(k_{A\rightarrow}k_{B\rightarrow} - k_{A\leftarrow}k_{B\leftarrow}\right) \tag{12}$$

As was stated above, according to the second law of thermodynamics, if the field is not applied, there should be no preferential direction for the molecular diffusion and hence j_{av} must be equal to zero. Let us verify that this is indeed the case. Indeed, without the field, see Fig. 1, we have

$\Delta_1^0 + \Delta_4^0 = \Delta_2^0 + \Delta_3^0$, leading immediately to the identity

$$k_{A\rightarrow}^0 k_{B\rightarrow}^0 = k_{A\leftarrow}^0 k_{B\leftarrow}^0. \tag{13}$$

This expression is easy to understand: we have the overall rate for molecules moving to the right, $k_{A\rightarrow}^0 k_{B\rightarrow}^0$, equal to the rate, $k_{A\leftarrow}^0 k_{B\leftarrow}^0$, for them to move to the left. As a result, $j_{av} = 0$ exactly. Hence, indeed the unidirectional motion is *not* expected at equilibrium, a well-known result[3,9–11] trivially confirmed in our simple theory.

In fact, in this case we can get at long times the *detailed balance* condition, $k_B^0 p_B = k_A^0 p_A$, directly from Eqs. (3). Moreover, using the explicit expressions for the rates, one obtains:

$$\frac{p_A}{p_B} = \frac{k_B^0}{k_A^0} = \frac{\nu_B e^{-\beta E_B}}{\nu_A e^{-\beta E_A}} \tag{14}$$

where E_A and E_B are energies of states A and B. So, we have $p_A \sim e^{-\beta E_A}$ and $p_B \sim e^{-\beta E_B}$, which are the canonical distributions for these states valid at equilibrium, as expected.

When a constant field is applied, Eq. (12) gives the exact result for the flux. Using identity (13) and expressions for the rates given in section Theory, it can also be rewritten explicitly as

$$j_{av} = 2k_{A\rightarrow}^0 k_{B\rightarrow}^0 \frac{e^{2\lambda} - e^{-2\lambda}}{(k_{A\rightarrow}^0 + k_{B\rightarrow}^0)\, e^{\lambda} + (k_{A\leftarrow}^0 + k_{B\leftarrow}^0)\, e^{-\lambda}} \tag{15}$$

where $\lambda = E\beta a/4$ is a constant. It is seen that the average current is not antisymmetric with respect to the change of the direction of the field, $j_{av}(E) \neq -j_{av}(-E)$. Only in the case of a weak external field, $\lambda \ll 1$, do we have the current

$$j_{av} \simeq \frac{2\beta a E}{\kappa_0} k_{A\leftarrow}^0 k_{B\leftarrow}^0 \tag{16}$$

that is exactly antisymmetric, $j_{av}(E) = -j_{av}(-E)$, since the flux is proportional to the field. Also, for the zero field, $\lambda = 0$, we immediately obtain $j_{av} = 0$.

As an illustration, the net current for the BIPEB molecule is shown in Fig. 2 as a function of the field. One can see that indeed the current is not exactly antisymmetric with respect to the

field, which is a consequence of the PES waveform being asymmetric.

Overall, the obtained result is trivially expected: if the field tilts the PES in one direction, all identical molecules will move in the same direction.

Sinusoidal field

Consider now a more interesting case of the time-periodic sinusoidal external field $E(t) = A\sin(\omega t)$. In this case the full calculation cannot be performed analytically. However, usually the external field is considered weak. In this case an analytical calculation is in fact possible via an appropriate Taylor expansion. As a small parameter, we consider here the constant parameter $\lambda = A\beta a/4$. The condition of $\lambda \ll 1$ corresponds to the energy aA being small with respect to the thermal energy, $k_B T$.

We shall expand in the Taylor series with respect to λ all the exponentials in Eqs. (5)-(10) limiting ourselves with the terms up to the second order, and perform the integrations analytically. Then, a rather simple but cumbersome calculation for the probability (5) yields:

$$p_A(t) = p_A^{(0)}(t) + p_A^{(1)}(t) + p_A^{(2)}(t) + O\left(\lambda^3\right) \tag{17}$$

where

$$p_A^{(0)}(t) = e^{-\kappa_0 t} + \frac{k_B^0}{\kappa_0}\left(1 - e^{-\kappa_0 t}\right) \tag{18}$$

is the zero order contribution,

$$p_A^{(1)}(t) = \frac{\lambda\kappa_1^0}{\omega}\left(\cos(\omega t) - 1\right)e^{-\kappa_0 t} + \frac{\lambda\Delta k_B^0}{\omega^2 + \kappa_0^2}\left[\omega e^{-\kappa_0 t} - \omega\cos(\omega t) + \kappa_0\sin(\omega t)\right]$$

$$+\frac{\lambda\kappa_1^0 k_B^0}{\omega\kappa_0}\left(1 - e^{-\kappa_0 t}\right)\cos(\omega t) - \frac{\lambda k_B^0\kappa_1^0}{\omega\left(\omega^2 + \kappa_0^2\right)}\left[-\kappa_0 e^{-\kappa_0 t} + \omega\sin(\omega t) + \kappa_0\cos(\omega t)\right] \tag{19}$$

is the first order, and

$$p_A^{(2)}(t) = \lambda^2 e^{-\kappa_0 t}\left\{\frac{\kappa_1^0}{\omega^2\left(\omega^2 + \kappa_0^2\right)}\left(\Delta k_B^0\omega^2 + k_B^0\kappa_0\kappa_1^0\right)\cos(\omega t) - \frac{\kappa_1^0}{4\omega^2\left(4\omega^2 + \kappa_0^2\right)}\left(4\Delta k_B^0\omega^2 + k_B^0\kappa_0\kappa_1^0\right)\right.$$

$$+\frac{1}{4}\left(k_B^0-\kappa_0\right)\left(t-\frac{\sin\left(2\omega t\right)}{2\omega}\right)-\frac{k_B^0}{4\kappa_0}\left(\frac{\kappa_1^0}{\omega}\right)^2\left(2\cos^2\left(\omega t\right)+1\right)+\frac{1}{2}\left(\frac{\kappa_1^0}{\omega}\right)^2\left(\cos\left(\omega t\right)-1\right)^2\Bigg\}$$

$$+\lambda^2\Bigg\{-\frac{k_B^0\left(\omega^2-\left(\kappa_1^0\right)^2\right)}{4\omega^2\left(4\omega^2+\kappa_0^2\right)}\left(2\omega\sin\left(2\omega t\right)+\kappa_0\cos\left(2\omega t\right)\right)+\frac{k_B^0}{8\omega}\sin\left(2\omega t\right)$$

$$-\frac{4\Delta k_B^0\kappa_1^0+k_B^0\kappa_0}{8\omega\left(4\omega^2+\kappa_0^2\right)}\left(-2\omega\cos\left(2\omega t\right)+\kappa_0\sin\left(2\omega t\right)\right)+\frac{k_B^0}{4\kappa_0}\left(\frac{\kappa_1^0}{\omega}\right)^2\left(2\cos^2\left(\omega t\right)+1\right)$$

$$+\frac{\kappa_1^0}{\omega^2\left(\omega^2+\kappa_0^2\right)}\left[\Delta k_B^0\omega\left(-\omega\cos\left(\omega t\right)+\kappa_0\sin\left(\omega t\right)\right)-k_B^0\kappa_1^0\left(\omega\sin\left(\omega t\right)+\kappa_0\cos\left(\omega t\right)\right)\right]\cos\left(\omega t\right)\Bigg\} \quad (20)$$

is the second order contribution. The following new combinations of the rates have been introduced:

$$\kappa_1^0=\Delta k_B^0+\Delta k_A^0=\left(k_{B\rightarrow}^0-k_{B\leftarrow}^0\right)+\left(k_{A\rightarrow}^0-k_{A\leftarrow}^0\right) \quad (21)$$

with $\Delta k_B^0=k_{B\rightarrow}^0-k_{B\leftarrow}^0$ and $\Delta k_A^0=k_{A\rightarrow}^0-k_{A\leftarrow}^0$.

As we are interested in the net current at long times, the exponentially decaying terms in the expressions above can be omitted. Expanding the rates in Eq. (8) up to the second order with respect to λ as well and substituting there terms from $p_A(t)$ that remain at long times, we obtain after some lengthy but simple algebra the current as a sum of three contributions. In the zeroth order

$$j^{(0)}(t)=\Delta k_B^0+\frac{k_B^0}{\kappa_0}\left(\Delta k_A^0-\Delta k_B^0\right)=\frac{2}{\kappa_0}\left(k_{B\rightarrow}k_{A\rightarrow}-k_{B\leftarrow}k_{A\leftarrow}\right)=0 \quad (22)$$

i.e. we obtain a zero contribution. The identity (13) has been used in the last passage. This result is to be expected as in this order of the theory the situation is equivalent to having no external field; this also corresponds to the situation of Eq. (12) and the zero field.

The expression for the current in the first order reads, in the long time limit:

$$j^{(1)}(t)=\lambda\left[k_B^0+\frac{k_B^0}{\kappa_0}\left(k_A^0-k_B^0\right)\right]\sin\left(\omega t\right)+p_A^{(1)\infty}(t)\left(\Delta k_A^0-\Delta k_B^0\right) \quad (23)$$

where $k_A^0=k_{A\rightarrow}^0+k_{A\leftarrow}^0$ and $p_A^{(1)\infty}(t)$ is the part of the expression in Eq. (19) that survives at long

times. It is easy to see that the terms that remain at long times in Eq. (19) for $p_A^{(1)\infty}(t)$ are all proportional to sine and cosine functions of ωt. Consequently, the whole expression for the current (23) in the first order contains only terms proportional to these functions. Hence, when averaging the expression for the current via Eq. (10) over the period $\mathcal{T} = 2\pi/\omega$ of the external sinusoidal field, the total contribution to the average current from the first order with respect to λ vanishes, $j_{av}^{(1)}(t) = 0$.

Therefore, at long times the first non-vanishing term is of the second order:

$$j^{(2)}(t) = \frac{\lambda^2}{2}\sin^2(\omega t)\, j^{(0)}(t) + \lambda p_A^{(1)\infty}(t)\left(k_A^0 - k_B^0\right)\sin(\omega t) + p_A^{(2)\infty}(t)\left(\Delta k_A^0 - \Delta k_B^0\right) \tag{24}$$

where $p_A^{(2)\infty}(t)$ is the part of Eq. (20) that survives at long times. Substituting the obtained expression into Eq. (10) and averaging over the period $\mathcal{T}$ of the field, one obtains the final expression for the net flux:

$$j_{av}^{(2)} = \frac{4\lambda^2\kappa_0^2}{\kappa_0^2 + \omega^2} K_{asymm} \tag{25}$$

Here we defined a quantity of special interest, the asymmetry coefficient,

$$\begin{aligned} K_{asymm} &= \frac{1}{\kappa_0^3}\left(k_{B\rightarrow}^0 k_{A\leftarrow}^0 - k_{A\rightarrow}^0 k_{B\leftarrow}^0\right)\left(k_{A\rightarrow}^0 k_{A\leftarrow}^0 - k_{B\rightarrow}^0 k_{B\leftarrow}^0\right) \\ &= \frac{1}{\kappa_0^3}\frac{k_{A\leftarrow}^0}{k_{B\leftarrow}^0}\left(\left(k_{B\rightarrow}^0\right)^2 - \left(k_{B\leftarrow}^0\right)^2\right)\left(\left(k_{A\rightarrow}^0\right)^2 - \left(k_{B\leftarrow}^0\right)^2\right) \end{aligned} \tag{26}$$

that only depends on the shape of the PES waveform. Identity (13) has been used in the second passage. The obtained expression is the leading term in the total net flux for the sinusoidal external field.

The current is proportional to the asymmetry coefficient that contains a product of two terms in the brackets. These terms may each change their sign depending on the shape of the PES waveform thereby affecting the overall sign of the current (and hence the direction of the net flux). To facilitate our analysis, it is convenient, using explicit expressions for the rates, to rearrange the asymmetry coefficient:

$$K_{asymm} = \frac{\nu^2}{\kappa_0^3} k^0_{A\leftarrow} k^0_{B\leftarrow} \left(e^{-2\beta E_{TS_2}} - e^{-2\beta E_{TS_1}}\right)\left(e^{2\beta E_A} - e^{2\beta E_B}\right) \tag{27}$$

It is seen then that K_{asymm} vanishes if either the energies at the minima, $E_A = E_B$, or the energies of the transition states, $E_{TS_1} = E_{TS_2}$ (see Fig. 1), are equal. Hence, at this level of theory there is no current if the PES waveform possesses this spatial symmetry. It is also interesting to notice, that only one (any) of these two conditions is sufficient for the current to vanish.

The other point worth discussing is the direction of the current. It is determined exclusively by the sign of the asymmetry coefficient, which, in turn, is defined by the combined sign of the two brackets in Eqs. (26) or (27). To simplify our analysis, let us assume that $E_A < E_B$ (one can always choose the lower of the two minima to be A), so that the second bracket is negative. Therefore, the direction of the net current is basically determined by the relative values of the transition states energies: if $E_{TS_1} < E_{TS_2}$, then $K_{asymm} > 0$ and the current flows to the right, while if $E_{TS_1} > E_{TS_2}$ the asymmetry coefficient $K_{asymm} < 0$ and it flows to the left. The full dependence of the asymmetry coefficient on the shape of the PES waveform is shown in Fig. 3(a), clearly demonstrating the areas of positive (red) and negative (blue) regions. The expected increase of K_{asymm} with temperature is demonstrated for the BIPEB molecule in Fig. 3(b).

Clearly, molecules that are not symmetric upon a 180° rotation about a vertical axis and with their PES waveforms related to each other by a mirror reflection in a plane perpendicular to the Cu rows and the surface, will diffuse in opposite directions along the rows, when oriented differently [16].

The dependence of the net current on the frequency of the field and on the temperature are shown in Fig. 4 for both the analytical and (exact) numerical calculations. It can be seen that the analytical formula (25) yields almost exact results for the amplitudes $A \preceq 0.02$ eV; deviations from the exact result start to be noticeable at larger amplitudes (stronger external fields). However, even for large A values the general trend of the current is correctly reproduced for both dependencies by our analytical result obtained in the second order with respect to the field: the current is the largest in the limit of the slowly changing field, $\omega \to 0$, reaching the value of $j_{av}\,(\omega \to 0) = 4\lambda^2 K_{asymm}$, and then decaying to zero at larger frequencies as $1/\omega^2$, while the current increases with temperature, as expected. Concerning the latter dependence, it appears that, compared to the exact results, at

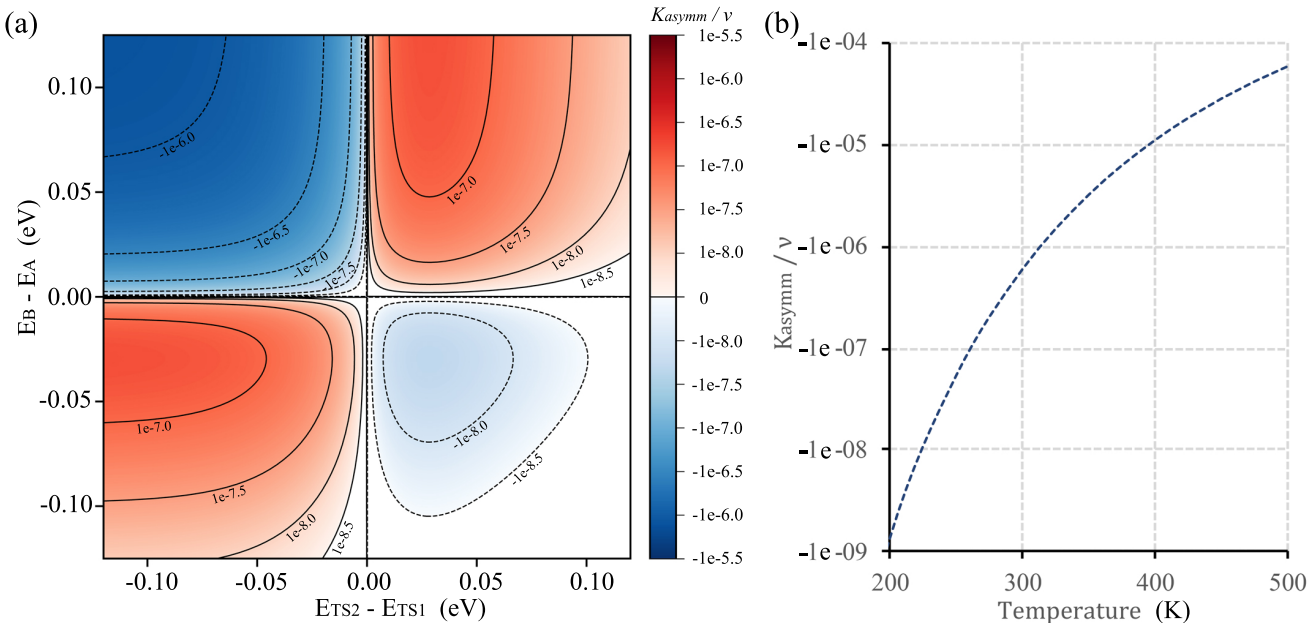

Figure 3: The asymmetry coefficient (in units of ν) of Eq. (27) as a function of (a) the shape of the PES waveform at T =300 K and (b) temperature for the BIPEB molecule.

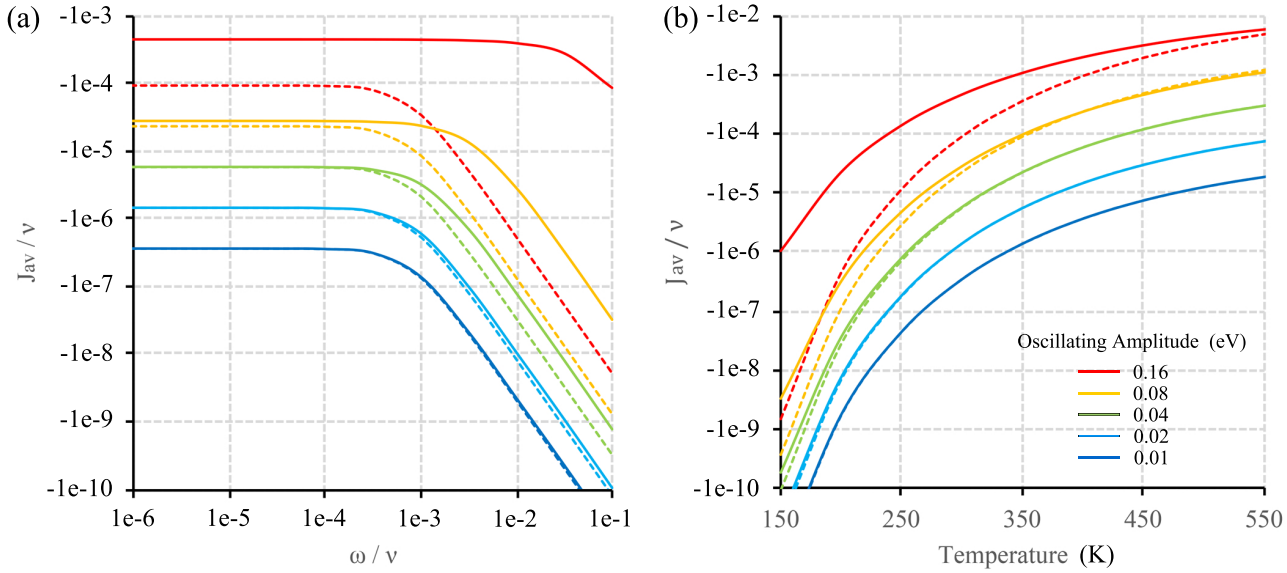

Figure 4: Dependence of the average current (in units of the rate prefactor ν) on the (a) frequency ω (at T =300 K, also in units of ν) and (b) temperature T (at $\omega = 10^{-7}\nu$) for the sinusoidal external field $E = A\sin(\omega t)$ for several oscillation amplitudes A (as indicated). Full curves correspond to the numerical solution of the rate equations and therefore represent exact results valid for any field strength (oscillation amplitudes). Dashed lines correspond to the analytical result of Eq. (25) that is valid for weak fields (small amplitudes).

small T the current is underestimated by the analytical result and the T dependence is steeper towards higher T than it should be.

Shifted sinusoidal field

Here we shall consider the external field of the form $E(t) = A\left[\sin\left(\omega t\right) + \delta\right]$ with a constant shift defined by the dimensionless constant $0 \leq \delta < 1$. This external stimulus combines an oscillating and constant contributions.

A calculation similar to that for the sinusoidal field gives the same expression (18) for the zero order probability. The first and second order expressions valid at long times are obtained, after some trivial but tedious calculations, as:

$$p_A^{(1)\infty}(t) = \frac{\Delta k_B^0 \kappa_0 - k_B^0 \kappa_1^0}{\kappa_0^2\left(\kappa_0^2 + \omega^2\right)}\left[\delta\left(\kappa_0^2 + \omega^2\right) + \kappa_0\left(-\omega\cos\left(\omega t\right) + \kappa_0 \sin\left(\omega t\right)\right)\right] \tag{28}$$

and

$$\begin{aligned} p_A^{(2)\infty}(t) = \frac{\lambda^2}{2}\frac{\kappa_1^0\left(-\Delta k_B^0\kappa_0 + k_B^0\kappa_1^0\right)}{\kappa_0^3\left(\kappa_0^2+\omega^2\right)^2\left(\kappa_0^2+4\omega^2\right)}\Big\{&\left(\kappa_0^2+\omega^2\right)\left(\kappa_0^2+4\omega^2\right)\left(\kappa_0^2+2\delta^2\left(\kappa_0^2+\omega^2\right)\right) \\ &-2\omega\delta\kappa_0\left(\kappa_0^2+4\omega^2\right)\left(3\kappa_0^2+\omega^2\right)\cos\left(\omega t\right) + \kappa_0^2\left(2\omega^4+\omega^2\kappa_0^2-\kappa_0^4\right)\cos\left(2\omega t\right) \\ &+4\delta\kappa_0^4\left(\kappa_0^2+4\omega^2\right)\sin\left(\omega t\right) - 3\omega\kappa_0^3\left(\kappa_0^2+\omega^2\right)\sin\left(2\omega t\right)\Big\} \end{aligned} \tag{29}$$

The 0-th order current vanishes again; however, the first order current is not zero. In fact, it is the leading term in this case. Its expression, after time averaging, reads:

$$j_{av}^{(1)} = \frac{8\lambda\delta}{\kappa_0}k_{A\leftarrow}^0 k_{B\leftarrow}^0 = \frac{8\lambda\delta}{\kappa_0}k_{A\rightarrow}^0 k_{B\rightarrow}^0 \tag{30}$$

Assuming $\lambda = A\beta a/4 > 0$, this expression for the current is positive for any values of the rates (and hence for any shape of the PES waveform). Also note that this expression coincides with Eq. (16) for the case of the constant field since $8\lambda\delta = 2\beta a\left(A\delta\right)$, where $A\delta$ is the constant component of the shifted sinusoidal field.

The current in this order of our theory is proportional to δ and hence must be small for $\delta \ll 1$. Hence, it is still necessary to consider the second order term, for which we obtain:

$$j_{av}^{(2)} = \xi \frac{4\lambda^2 \kappa_0^2}{\kappa_0^2 + \omega^2} K_{asymm} \tag{31}$$

where the factor $\xi = 1 + 2\delta^2 + 2\left(\omega\delta/\kappa_0\right)^2$. It is by this very factor the obtained expression for the shifted sinusoidal field differs from formula (25) we obtained for the purely sinusoidal field. For small δ this factor is close to one and the two expressions become practically identical. Still, the relatively small first order contribution makes the difference as will be seen shortly when the numerical results are discussed. As follows from Fig. 5, the analytical solution serves as a good approximation for the amplitudes $A \preceq 0.015$ eV; at larger amplitudes and larger shift parameters deviations from the exact numerical solutions become significant.

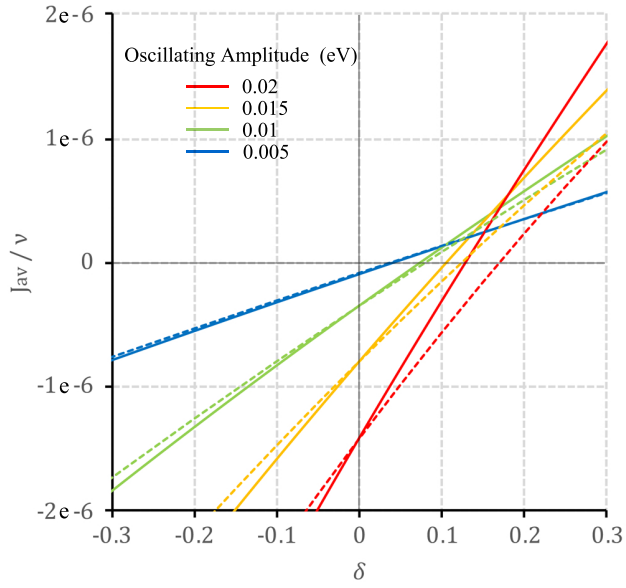

Figure 5: Dependence of the average current (in units of the rate prefactor ν) on the shift parameter δ at T =300 K and $\omega = 10^{-7}\nu$ for the sinusoidal external field $E = A\left[\sin\left(\omega t\right) + \delta\right]$ for several oscillation amplitudes A (as indicated). Full curves correspond to the numerical solution of the rate equations and therefore represent exact results valid for any field strength (oscillation amplitudes), while dashed lines correspond to the analytical result obtained by the sum of the contributions from Eqs. (30) and (31) that is valid for weak fields (small amplitudes).

Qualitatively, the constant field contribution (30) pushed the molecules to the right or left depending on the sign of the shift parameter δ, while the oscillating component of the field (31)

pushes the molecules into one or another direction depending on the sign of the asymmetry coefficient, K_{asymm}, i.e. according to the shape of the PES waveform. Both these factors, applied together, determine the net current direction for the given molecule, $j_{av} = j_{av}^{(1)} + j_{av}^{(2)}$. In particular, a value of δ exists, δ_0, at which the two terms cancel each other leading to the zero net current. For $\delta > \delta_0$ and $\delta < \delta_0$ the currents have opposite directions, as shown in Fig. 6(a). The value of $a\delta_0 A$ increases with the increase of the oscillation amplitude (see also Fig. 7(d) for the dependence of δ_0 alone). We also observe that the current increases with the oscillation amplitude A, as expected. Importantly, for the given PES, changing the value of the constant field, $A\delta$, one can change the direction of the net current.

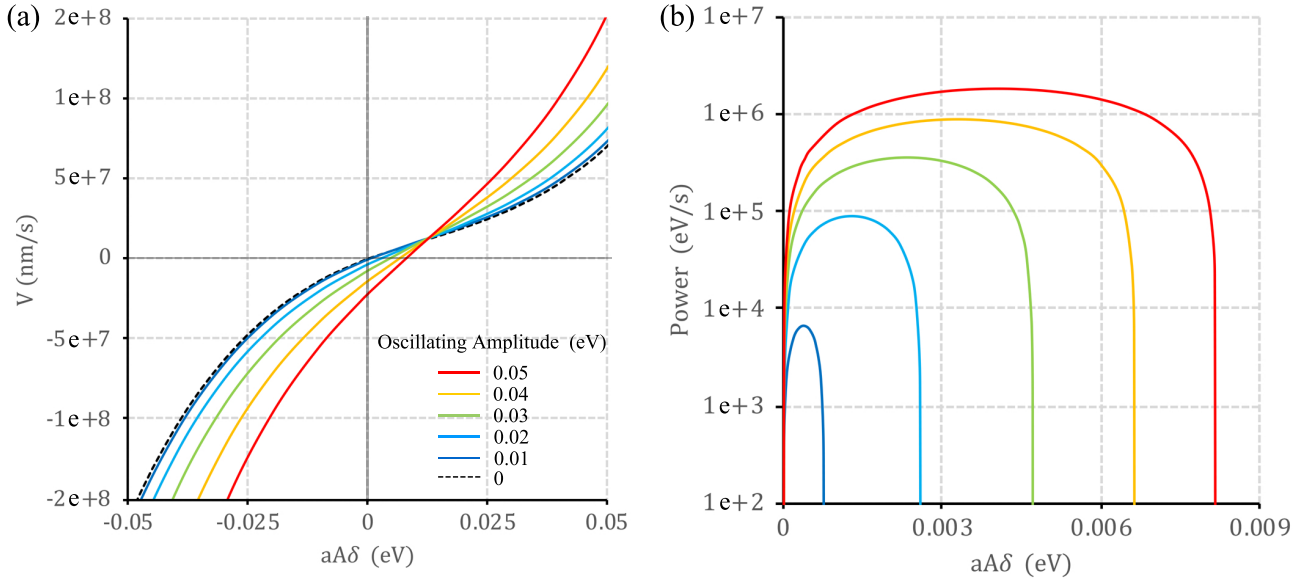

Figure 6: (a) The net current, in units of ν, and (b) the accumulated power (in eV/s) of the BIPEB molecules under the shifted sinusoidal field at T =300 K and $\omega = 10^{-7}\nu$ as a function of the constant field shift $aA\delta$ (in eV), both calculated by solving numerically the rate equations. The dashed line in (a) corresponds to applying only the constant field ($E = A\delta$).

An interesting question would be whether energy can be extracted from Brownian particle driven by an oscillating field of zero mean. Here, Eq. (31) also decribes the motion of Brownian motor driven by an sinusoidal field with oscillation amplitude A against external load $A\delta$. The average power P generated by the diffusing BIPEB molecules was calculated and shown in Fig. 6(b), where $P = j_{av}\Delta U$ and $\Delta U = aA\delta$ is the change of the potential energy of the molecule after diffusing by one lattice constant. At given oscillation amplitude, the power output increases when

the load increases before it reaches a maximum and then starts falling back to zero. At heavier load, a greater oscillation amplitude would be required for the Brownian motor to function as expected.

Resolution of chiral molecules

Above we have considered, using both the exact numerical and the approximate analytical methods, the behaviour of the molecular net current for various parameters, such as the shape of the PES of the molecule, the type and strength of the external field, and the temperature. We find that at certain conditions the identical molecules would move preferentially unidirectionally in one or the other direction. When a constant and a sinusoidal fields are applied at the same time, the signs of both the constant component and of the asymmetry coefficient K_{asymm} determine the eventual direction in which molecules would move. An interesting question is whether, given two different types of molecules being present on the surface (i.e. of different PES waveforms), it would be possible to find a field upon which the molecules can be separated, i.e. when one type of molecules moves to the right and the other to the left.

We found above that under a sinusoidal field different molecules would move in opposite directions if their asymmetry coefficients (determined by the shapes of their respective PES waveforms) have different signs (otherwise, they would move in the same direction, albeit at different speeds). If the oscillating field has a shift component, however, the diffusion in opposite directions is possible by a careful choice of the field. The BIPEB molecule considered so far actually has two enantiomers, R and S. The calculations presented above were done only for the R enantiomer. To illustrate a possibility of the separation of different molecules, we shall compare here the diffusion of the enantiomer R and the conformer S* of the second enantiomer[16], both shown in Fig.7(a). Their PES shown in Fig. 7(b) were calculated[16] to be only slightly different, with the energy barriers of S* being Δ_1^0 =0.320 eV, Δ_2^0 =0.285 eV, Δ_3^0 =0.181 eV and Δ_4^0 =0.146 eV (compare with the values given for R in section Theory).

The numerically calculated net currents for R (solid lines) and S* (dashed lines) are shown in Fig. 7(c). At $\delta = 0$ both enantiomers go to the left. However, one can see that there exist such

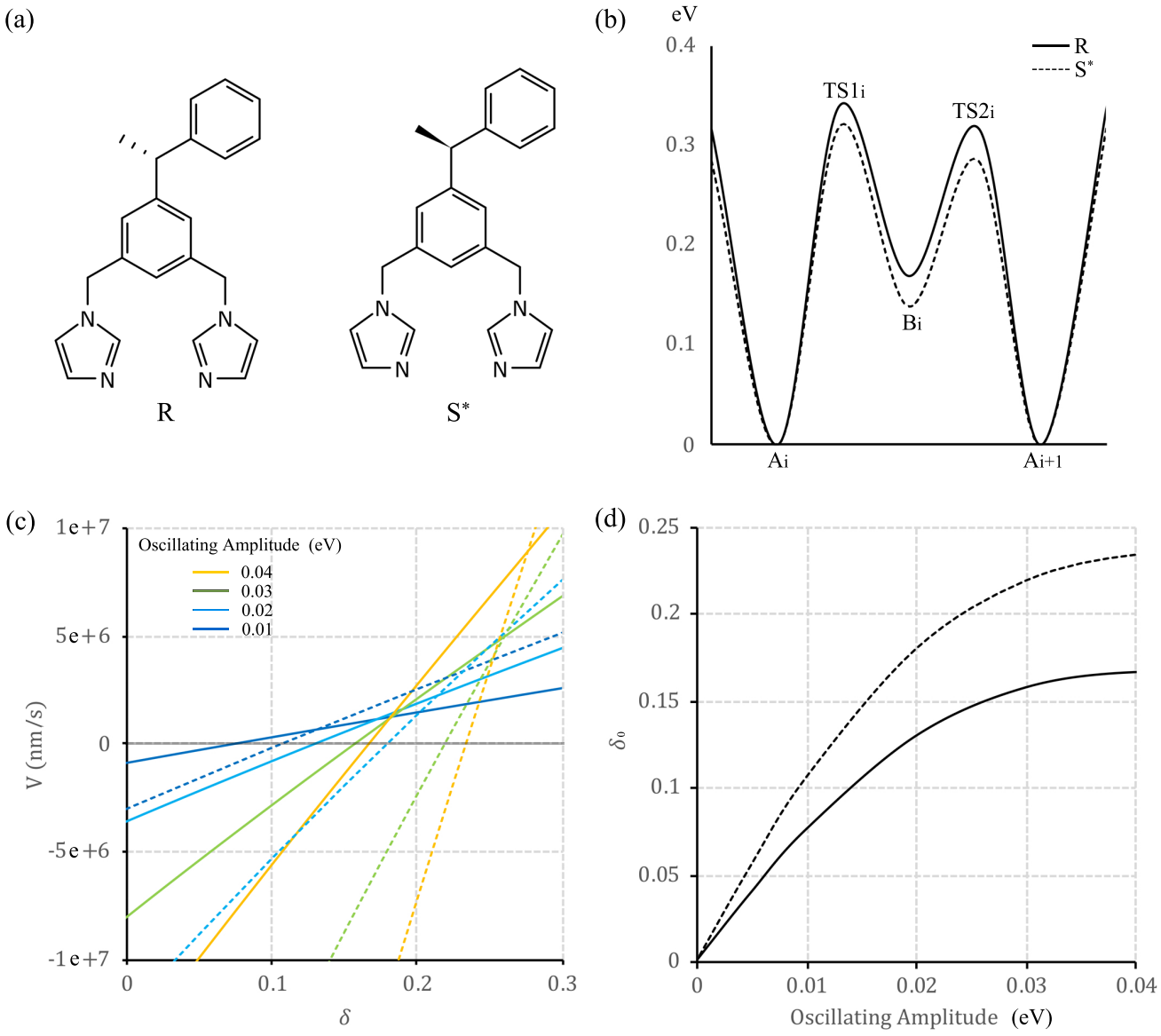

Figure 7: Comparison of the diffusion of two enantiomers, R and S*, of the BIPEB molecule. (a) The two enantiomers and (b) their PES[16]. (c) The net current (in units of ν) for R (solid lines) and S* (dashed lines) for a few values of the oscillation amplitude. (d) The dependence of the shift parameter δ_0 (yielding the zero current) on the oscillation amplitude A for R (solid lines) and S* (dashed lines). The results in (c,d) were obtained by numerically solving the rate equations for T =300 K and $\omega = 10^{-7}\nu$.

values of the shift parameter $\delta > 0$ for which the signs of the currents for the two enantiomers are different. This becomes especially obvious from panel (d) in which the value of δ_0 is shown as a function of the amplitude A of the oscillating field. Since for $\delta > \delta_0$ a molecule would preferentially move to the right and for $\delta < \delta_0$ to the left, for the given oscillating amplitude, A, the values of the shift parameter δ lying between the solid and the dashed curves would ensure the R and S* enantiomers to move preferentially in opposite directions.

Conclusions

Concluding, in this work we have considered, both numerically and analytically, the 1D diffusion of molecules with a double-peak PES on a periodic crystalline surface under external stimuli. The BIPEB molecule on the Cu(110) surface (a bipedal walker diffusing along the Cu rows) has been considered as a specific example of Brownian motor driven by oscillating field. We find that both the application of an external stimulus (either an electrostatic field or temperature gradient) to break thermal equilibrium and an asymmetry of the PES of the molecule on the surface are the necessary ingredients for the unidirectional motion, in complete agreement with previous studies[3,9–11]. Our calculations show that a constant field would provide the unidirectional motion for molecules with different PES, an oscillating field of zero mean may only separate the molecules if the asymmetry coefficients of their PES are of different sign (one molecule has the first peak in its PES higher than the second and the other way round for the second molecule), while the shifted oscillating field is capable of separating two molecules on the surface even if their PES are quite similar. This study can be easily generalised to more complex PES containing more than two peaks in the PES waveform.

Our simple rate equation method based on known PES waveforms of the molecules, that can routinely be calculated nowadays using *ab initio* methods, can be applied to realistic molecules and surfaces. For weak fields (the case most likely in practical applications) an analytical result is available for sinusoidal and shifted sinusoidal fields, which enable one to analyse different molecules without performing any numerical kinetic calculations in terms of their possible unidirectional motion. In the cases of strong fields or fields for which the analytical solution is problematic, it is

demonstrated that trivial and cheap numerical simulations of the developed kinetic equations are routinely possible. Conversely, one may wish to synthesize molecules in such a way that, apart from a useful function they are designed for, they would also possess the desired diffusion PES that corresponds to the specific stimuli to be applied ensuring their unidirectional motion. The formulae developed above may prove to be useful in this case.

We hope that this paper will be useful for researchers working in the field of molecular surface physics and chemistry, and that it would stimulate further studies, especially experimental ones, aiming at providing unidirectional diffusion of molecules on surfaces using the considered Brownian ratchet mechanism.

Acknowledgement

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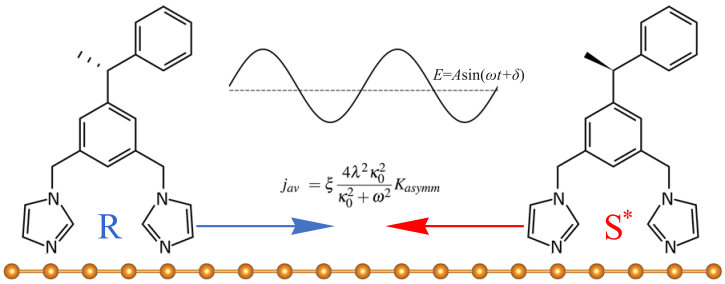

Separating Chiral Molecules using Oscillating Field